

(19) Korea patent office (KR) Unexamined Patent  
Publication (A)

(51) Int.Cl. 6 H01L 21/31

Registration No	KR2002-0032054.
Application No	10-2000-0062930
Application Date	25/10/2000
Publication Date	03/05/2002
Agent	SHINSUNG PATENT FIRM
Inventor	Heung-Jae Cho
	Chan Im
	Dae-Gyu Park
Applicant	Hynix Semiconductor Inc. Jong-Seop Park
Examination	EopEum
Title of Invention	The method for forming silicate [Method for forming silicate by using atomic layer deposition] using the atomic layer deposition.

## \* Legal Status

Date of request for an examination	20050929
Notification date of refusal decision	00000000
Final disposal of an application	registration
Date of final disposal of an application	20070129
Patent registration number	1006937810000
Date of registration	20070306
Number of opposition against the grant of a patent	
Date of opposition against the grant of a patent	00000000
Number of trial against decision to refuse	
Date of requesting trial against decision to refuse	
Date of extinction of right	



## Abstract

The present invention relates to the method for forming silicate it can improve the interfacial property of a silicate and silicon substrate and it prevent the GOI characteristic degradation according to that, and for obtaining the step coverage property of being excellent. In the embodiment of the present invention, a source including H<sub>2</sub>O, O, Si etc. is gradually, by stages injected and the Hf silicate is formed into the method for atomic layer deposition. The method for performing a sequential heat treatment in order to improve the membranous property of the

Hf silicate is shown.



#### Representative Drawing(s)

Fig. 2d



#### Keyword(s)

The silicate, atomic layer deposition, hf, thermal process.



#### Description

##### ■ Brief Explanation of the Drawing(s)

Figure 1 is a structure chart of the zirconium silicate which the Hf silicate type processing sectional view, and fig. 3 have the structure of being similar to the Hf silicate according to the cross-sectional view showing the structure of the reaction chamber used for the silicate formation process of the present invention, and the figs. 2a through 2d is the embodiment of the present invention.

##### ■ Details of the Invention

##### ■ Purpose of the Invention

##### ■ The Technical Field to which the Invention belongs and the Prior Art in that Field

The present invention relates to the semiconductor element manufacture field, particularly, to the method of forming a gate dielectric layer of the MOS transistor.

In the integrated of the semiconductor device, the thickness of the gate insulating layer \*\*\*s to an improvement. Because the leakage current is enlarged with the direct tunneling through the gate insulating layer if the gate insulating layer \*\*\*s, the gate insulating layer is formed into the material in which recently the dielectric constant is high. That is, many research about the method for reducing the leakage current by increasing the effective thickness of the gate insulating layer, proceeds. And the method for forming the Hf oxide film (HfO<sub>2</sub>) or the Hf silicate on the silicon substrate is suggested as the representative example.

As to HfO<sub>2</sub>, the threshold voltage of the transistor which is formed on the wafer in which the dielectric constant is changed according to the crystallographic orientation because of being crystallized at the low temperature is not fixed. Moreover, there is a problem that in the increment of the leakage current, and a deterioration and source of GOI it has the grain boundary, the phenomenon that becomes with the congestion (crowding) announces in the electric charge grain boundary moving towards a drain and in conclusion, an affect is given to the working speed of a device during.

On the contrary, as to the Hf silicate, the dielectric constant is lower than HfO<sub>2</sub>. However, because of remaining as the amorphous structure of being stabilized in the high temperature, it can overcome the problem that the Hf oxide film has. That is, the Hf silicate is no need to form the separate interlayer film stable and which can have the interfacial property of being stable with Si and considering the interfacial property than HfO<sub>2</sub>. It can form the

gate electrode into the doped polysilicon on the Hf silicate and it like that can use the conventional semiconductor process.

The conventional Hf silicate forms by using the physical vapor deposition. That is, Hf and Si each target are sputtered, or Hf and Si the sputtering (co-sputtering) and oxidation process are together performed and the Hf silicate is formed on the silicon substrate.

As to this conventional Hf method for forming silicate, because of using the method of physical vapor deposition, a silicate elementarily, primarily gets the plasma corruption (plasma damage) and the interfacial property of the Hf silicate and silicon substrate interface becomes bad and a problem is generated in the component performance. The trap charge (trapped charge) is generated within the Hf silicate and the problem that the GOI (gate oxide integrity) characteristic is degraded is generated. Moreover, the method of physical vapor deposition has the disadvantage that the thickness of the silicate which is evaporated in the element isolation region and active area because the step coverage characteristic is bad is respectively different and the GOI characteristic is lowered.

#### ■ The Technical Challenges of the Invention

The problem as described above is solved. And it are an object of the present invention to provide the method for forming silicate it can improve the interfacial property of a silicate and silicon substrate and it prevent the GOI characteristic degradation according to that, and for obtaining the step coverage property of being excellent.

#### ■ Structure & Operation of the Invention

The purpose as described above is achieved. And the present invention is to provide the method for forming silicate for alternately injecting the first element, and the oxygen and silicon each source as to the method for forming silicate for being made of the first element, and the oxygen and silicon within the reaction chamber and forming a silicate into the atomic layer deposition on a wafer.

Moreover, a purpose is accomplished. And the present invention is to provide the method for forming silicate for including the fourth stage forming the silicate consisting of the first step injecting a wafer within the reaction chamber, the second step injecting the first source, the third step injecting the second source, and the first element, and the compound of the silicon and oxygen the third source as to the method for forming silicate for being made of the first element, and the oxygen and silicon. As to the second step, the first element is included within the reaction chamber and deposits the first atomic layer by the atomic layer deposition on a wafer. As to the third step, the oxygen is included within the reaction chamber and forms the compound layer of the oxygen and the first element. As to the first element, and the compound of the silicon and oxygen the third source, the silicon is included is injected within the reaction chamber.

In the embodiment of the present invention, a source including H<sub>2</sub>O, O, Si etc. is gradually, by stages injected and the stable Hf silicate is formed into the atomic layer deposition method. The method for performing a sequential heat treatment in order to improve the membranous property of the Hf silicate is shown.

According to below, and the embodiment of the present invention, concretely it illustrates for the method for forming the Hf silicate on the silicon substrate dividing each domain from the element isolation film into the atomic layer deposition by the surface saturation mechanism.

As shown in Figure 1, the third source paths (101, 102, 103) through the first wears around the third source paths (101, 102, 103) through the first to the respective hotwires (heating line, 104) and it is wrapped. The silicon wafer (10) is mounted within the chamber (100) in which the reactive part (reaction part) is heated by thermal plates (heating block, 105). In fig. 1, the diagram symbol '200' shows the vacuum processing device, connected to the chamber that is, the pump etc.

Subsequently, as shown in it is seen in the drawing 2a, the Hf source including  $\text{HfCl}_4$  or the hafnium tetra-butoxide ( $\text{Hf}(\text{OC}_4\text{H}_9)_4$ ) etc. is put into 10 sccm or 10 slm extent reaction chamber (100). Hf is evaporated on the silicon wafer (10).

Subsequently, in order that the Hf source which does not react to the silicon wafer (10) and remains within the reaction chamber (100) is removed, the inactive gas of 10 sccm or 10 slm is injected within the reaction chamber (100) and the Hf source is discharged with the inactive gas from the reaction chamber (100).

Next, as shown in Figure 2b,  $\text{H}_2\text{O}$  or  $\text{O}_3$  is injected within the reaction chamber (100) or  $\text{O}_2$  or the  $\text{O}_3$  excited to the ultraviolet ray (UV) is injected with 10 sccm or about 10 slm and it reacts with the Hf already evaporated on the silicon wafer (10) and  $\text{HfO}_2$  is formed.

Subsequently, the inactive gas of 10 sccm or 10 slm is injected within the reaction chamber (100).  $\text{O}_2$  or the excited  $\text{O}_3$  is discharged to  $\text{H}_2\text{O}$  or the  $\text{O}_3$  which does not react to the silicon wafer (10) and remains within the reaction chamber (100), and the ultraviolet ray with the inactive gas from the reaction chamber (100).

Next, as shown in it is seen in the drawing 2c, the silicone compound including  $\text{SiH}_4$ ,  $\text{Si}_2\text{H}_6$  or the  $\text{SiCl}_2\text{H}_2$  etc. is injected into 10 sccm or 10 slm extent reaction chamber (100) and  $\text{HfO}_2$  and the Si already formed on the silicon wafer (10) are bound and the Hf silicate ( $\text{HfSi}_x\text{O}_y$ ) is formed.

Subsequently, the inactive gas of 10 sccm or 10 slm is injected within the reaction chamber (100). The  $\text{SiH}_4$ , which does not react to the silicon wafer (10) and remains within the reaction chamber (100)  $\text{Si}_2\text{H}_6$  or  $\text{SiCl}_2\text{H}_2$  etc. are discharged with the inactive gas from the reaction chamber (100).

Series of process to an exhaustion including the  $\text{SiH}_4$  in the Hf injection,  $\text{Si}_2\text{H}_6$  or  $\text{SiCl}_2\text{H}_2$  etc are repetitively performed and the Hf silicate layer of the constant thickness is formed.

Next, as shown in it is seen in the drawing 2d, the thermal process for the densification of the Hf silicate layer is performed. At this time, the method for doing for about half an hour with the rapid thermal processing (rapid thermal process) or the furnace annealing (furnace) and heat-treating the Hf silicate at  $500^\circ\text{C}$  or  $1000^\circ\text{C}$  temperature in the method, for exciting  $\text{O}_2$  or  $\text{O}_3$  and heat-treating the Hf silicate layer in  $300^\circ\text{C}$  or  $500^\circ\text{C}$  temperature by taking advantage of the ultraviolet ray  $\text{N}_2\text{O}$ , and  $\text{O}_2$  or the inert gas atmosphere can be used.

The Hf injection, the oxygen implanting, and the Si source implant step differentiate the order and it injects within the chamber and it can form the Hf silicate. In the meantime, the Hf silicate formation process progresses in the reaction chamber maintained by  $200^\circ\text{C}$  or  $800^\circ\text{C}$  temperature.

The subsequent processes of the etc. depositing the polysilicon layer or the metal layer etc. on a next, and the Hf silicate which as described above, is formed and performs the patterning process and forms the gate electrode of a transistor is progressed.

In the preferred embodiment of the present invention described in the above, the Hf method for forming silicate was explained. However, by using the Zr source like the  $\text{ZrCl}_4$ , Zr tetra-butoxide ( $\text{Zr}(\text{OC}_4\text{H}_9)_4$ ),  $\text{TaCl}_5$ , the Ta N thoxy ( $\text{Ta}(\text{OC}_2\text{H}_5)_5$ ),  $\text{LaCl}_3$  etc or the La source in order to form the zirconium silicate or the La silicate etc. instead of Hf, the various silicate in which the dielectric constant is high can be formed.

As described above, as to the present invention, by not using the method of physical vapor deposition and forming the Hf silicate it can prevent the damage according to the physical vapor deposition. Moreover, the Hf silicate having the composition which desires by appropriately controlling a dose including the  $\text{SiH}_4$ , which is the Si source  $\text{Si}_2\text{H}_6$  or  $\text{SiCl}_2\text{H}_2$  etc., can be formed.

Figure 3 is a structure chart of the zirconium silicate ( $\text{ZrSiO}_4$ ) having the structure of being similar to the Hf silicate ( $\text{HfSiO}_4$ ). It has the advantage which can form the silicate of the amorphous while controlling the dielectric constant by appropriately controlling amount of Si like the present invention in forming the Hf silicate ( $\text{HfSiO}_4$ ) in which the Hf silicate Hf and Si form O atom and bonding of the respective 4 as the structure where  $\text{HfO}_2$  and  $\text{SiO}_2$  are periodically connected like the zirconium silicate in each chain and having three dimensional structure. Moreover, the reliability of the gate insulating layer can be improved according to use the method for

atomic layer deposition with a superior step coverage property.

In the above, the present invention illustrated is not restricted by the above-described embodiment and the attached drawing, but it has to a person skilled in the art and it will be clear in the technical field in which the present invention belongs to be possible in the range that does not depart from the technical mapping of the present invention with many substitution, and the deformation and change like.

#### ■ Effects of the Invention

As described above, the present invention can prevent the preventing damage according to the physical vapor deposition by forming the Hf silicate into the method for atomic layer deposition. According to that, the gate insulating layer using the Hf silicate which has the high dielectric constant while the reliability is high and it is stable can be formed.



#### Scope of Claims

##### Claim 1 :

The method for forming silicate for alternately injecting the first element, and the oxygen and silicon each source as to the method for forming silicate for being made of first element, and the oxygen and silicon within the reaction chamber and forming a silicate into the atomic layer deposition on a wafer.

##### Claim 2 :

The method for forming silicate of the method for forming silicate for being made of the first element, and the oxygen and silicon comprising: the fourth stage forming the silicate consisting of the first step injecting a wafer within the reaction chamber, the second step injecting the first source, the third step injecting the second source, and the first element, and the compound of the silicon and oxygen the third source; as to the second step, the first element is included within the reaction chamber and deposits the first atomic layer by the atomic layer deposition on a wafer; as to the third step, the oxygen is included within the reaction chamber and forms the compound layer of the oxygen and the first element; and as to the first element, and the compound of the silicon and oxygen the third source, the silicon is included is injected within the reaction chamber.

##### Claim 3 :

The method for forming silicate of claim 2, further comprising the seventh step which more includes the fifth step injecting the inactive gas within the reaction chamber and discharges the first source remaining behind within the reaction chamber with the inactive gas from the reaction chamber after the second step; it more includes the sixth step injecting the inactive gas within the reaction chamber and discharges the second source remaining behind within the reaction chamber with the inactive gas from the reaction chamber after the third step; and it injects the inactive gas after the fourth stage within the reaction chamber and discharges the third source remaining behind within the reaction chamber with the inactive gas from the reaction chamber.

##### Claim 4 :

The method for forming silicate of claim 3, further comprising the eighth step which once more performs the second step or a series of process of being made of the seventh step after the seventh step at least.

##### Claim 5 :

The method for forming silicate of claim 4, further comprising the ninth step heat-treating a silicate after the eighth step.

Claim 6 :

The first element as to any one of claims 2 through 5.

The method for forming silicate wherein it is one among Hf, and Zr or La.

Claim 7 :

The first source as to claim 6.

The method for forming silicate wherein it is one among the  $\text{HfCl}_4$ , the hafnium tetra - butoxide ( $\text{Hf}(\text{OC}_4\text{H}_9)_4$ ), the  $\text{ZrCl}_4$ , Zr tetra - buta oxide ( $\text{Zr}(\text{OC}_4\text{H}_9)_4$ ),  $\text{TaCl}_5$ , the Ta N thoxy ( $\text{Ta}(\text{OC}_2\text{H}_5)_5$ ) or  $\text{LaCl}_3$ .

Claim 8 :

The method for forming silicate of any one of claims 2 through 5, wherein in the second step,  $\text{HfCl}_4$  or the hafnium tetra - butoxide ( $\text{Hf}(\text{OC}_4\text{H}_9)_4$ ) is injected and the Hf layer is formed on a wafer;  $\text{O}_2$  or the  $\text{O}_3$  excited to  $\text{H}_2\text{O}$  or  $\text{O}_3$ , and the ultraviolet ray in the third step is injected and it forms on a wafer with the  $\text{HfO}_2$  layer; and  $\text{SiH}_4$ , and  $\text{Si}_2\text{H}_6$  or  $\text{SiCl}_2\text{H}_2$  are injected in the fourth stage and the Hf silicate layer is formed on a wafer.

Claim 9 :

As to claim 8, by taking advantage of the ultraviolet ray, it excites  $\text{O}_2$  or  $\text{O}_3$  and the ninth step heat-treats a silicate in  $300^\circ\text{C}$  or  $500^\circ\text{C}$  temperature.

The method for forming silicate wherein in  $\text{N}_2\text{O}$ , and  $\text{O}_2$  or the inert gas atmosphere, it heat-treats at  $500^\circ\text{C}$  or  $1000^\circ\text{C}$  temperature with the rapid thermal processing or the furnace.



Drawings

Fig. 1

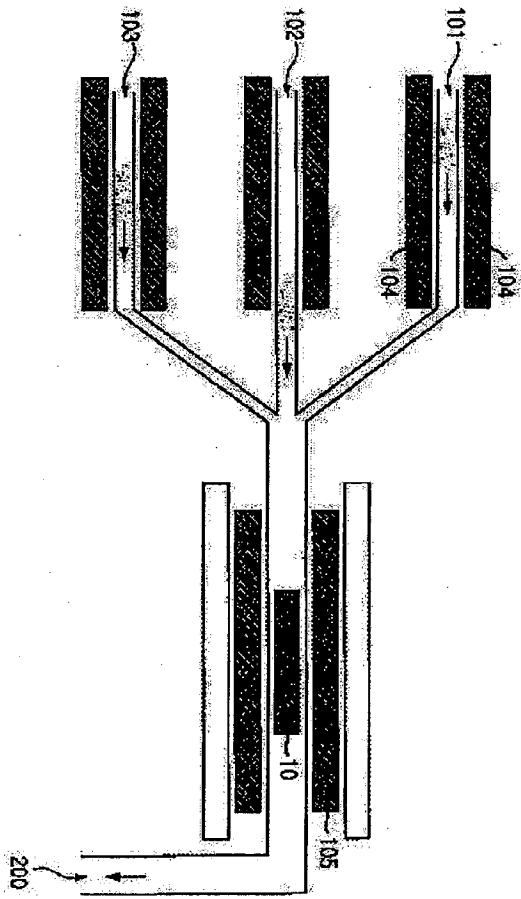


Fig. 2a

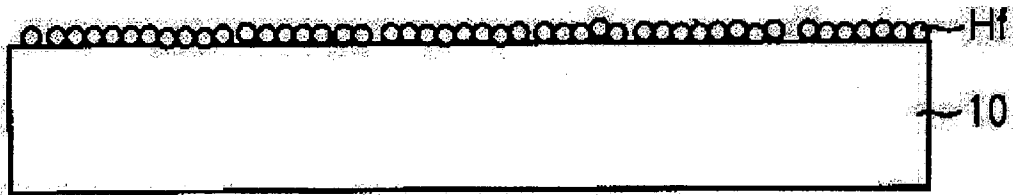


Fig. 2b

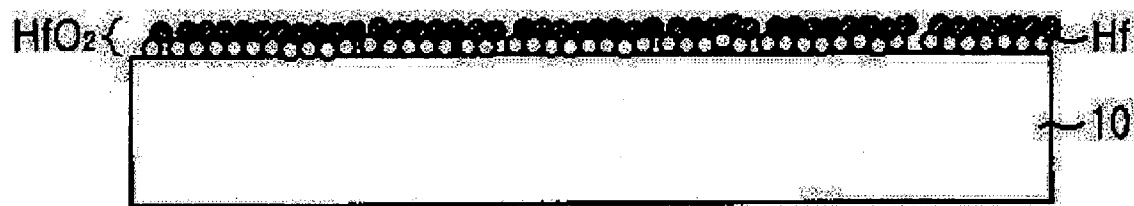


Fig. 2c

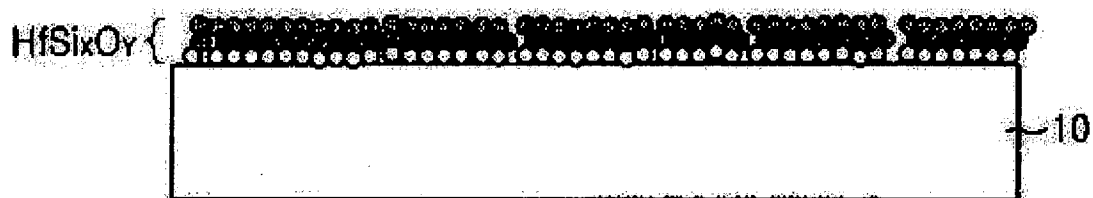


Fig. 2d

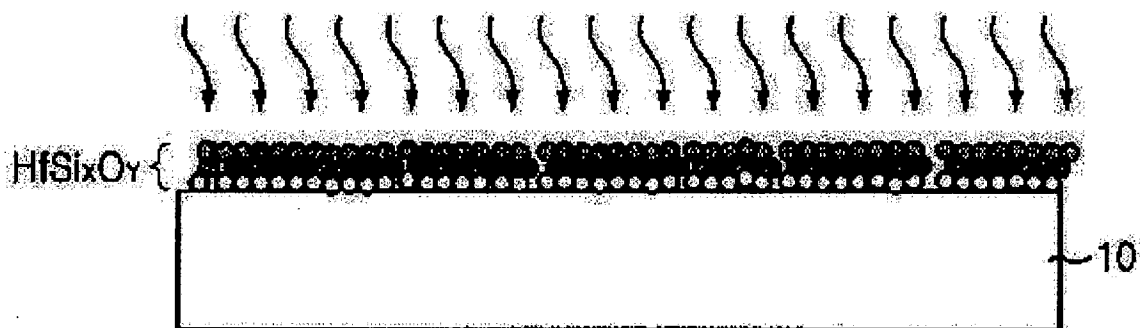


Fig. 3